Archaeal and bacterial tetraether lipids in tropical ponds with contrasted salinity (Guadeloupe, French West Indies): Implications for tetraether-based environmental proxies

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ABSTRACT

The occurrence and distribution of archaeal and bacterial glycerol dialkyl glycerol tetraether lipids (GDGTs) in continental saline environments have been rarely investigated. Here, the abundance and distribution of archaeal isoprenoid GDGTs (iGDGTs) and archaeol, and of bacterial branched GDGTs (brGDGTs) in four tropical water ponds of contrasting salinity in two islands from the French Western Indies, Grande-Terre and La Désirade, have been determined. The sedimentary distribution of the GDGTs strongly differed between the two islands. Caldarchaeol was largely predominant among iGDGTs in the (hyper)saline ponds from Grande-Terre, suggesting a substantial contribution of iGDGTs derived from methanogenic Archaea. In contrast, both caldarchaeol and crenarchaeol were present in high relative abundance in the low salinity ponds from La Désirade, suggesting that iGDGTs were derived from mixed archaeal communities. In addition, the relative proportion of the most methylated brGDGTs was much higher in Grande-Terre ponds than in La Désirade ponds. The applicability of different proxies based on GDGTs and archaeol was tested for these specific environments. The relative abundance of archaeol vs. caldarchaeol (ACE index) was

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comparable for the four ponds, independent of salinity, showing that the ACE might not necessarily track salinity change. Moreover, the relative proportion of caldarchaeol vs. total iGDGTs was unexpectedly observed to increase with salinity, suggesting production of this compound by halophilic Archaea. The supposed high abundance of methanogenic Archaea in Grande-Terre ponds prevented the application of TEX_{86} as a temperature proxy, whereas the TEX_{86} could be successfully used for local temperature reconstruction in La Désirade ponds. BrGDGTs seem to be produced predominantly in situ (water column and/or sediment) in hypersaline ponds from Grande-Terre, but in La Désirade ponds likely result from a mixture of soil and aquatic sources. In Grande-Terre ponds, brGDGT-derived temperature estimates generated using either soil or lacustrine calibrations were much lower than expected. The mismatch between expected and estimated temperature might be explained by the presence of halophilic microbial communities producing specific brGDGT distributions in the saline ponds from Grande-Terre. The study shows that the sources of brGDGTs, iGDGTs and archaeol (i) may strongly differ in aquatic environments of varying salinity, even at a regional scale, and (ii) have to be constrained before tetraether-derived proxies in such settings can be confidently applied.

Keywords: GDGTs; archaeol; salinity; environmental proxies; coastal ponds; Guadeloupe

1. Introduction

Glycerol dialkyl glycerol tetraethers (GDGTs) are complex lipids of high molecular weight (1000 Da), present in membranes of Archaea and some Bacteria. Archaeal membranes are formed predominantly of isoprenoid GDGTs (iGDGTs) with acyclic or ring-containing biphytanyl chains (Fig. 1). The iGDGTs occur ubiquitously in marine (Kim et al., 2008; Lipp and Hinrichs, 2009; Schouten et al., 2012) and lacustrine water columns and sediments (Sinninghe Damsté et al., 2009; Powers et al., 2010), as well as in peat and soil (Weijers et al., 2006a,b; Huguet et al., 2010a,b). One particular GDGT, crenarchaeol (VI; Fig. 1), contains one cyclohexane moiety and four cyclopentane moieties. It is biosynthesised by *Thaumarchaeota*, recently proposed as a new phylum within the domain Archaea (formerly known as Group I Crenarchaeota; Brochier-Armanet et al., 2008), even though it has been recently suggested that it could also be produced by Marine Group II *Euryarchaeota* (Lincoln et al., 2014). *Thaumarchaeota* are among the most abundant oceanic microorganisms (Karner et al., 2001; Agogué et al., 2008). Schouten et al. (2002) showed that the relative distribution of iGDGTs in *Thaumarchaeota* depends on environmental conditions, the number of cyclopentyl moieties increasing with sea surface temperature (SST). The correlation between the temperature at the surface of the oceans and the membrane lipid composition of *Thaumarchaeota* was expressed in the TEX_{86} index. Subsequent analysis of iGDGTs in a wide range of marine (e.g. Kim et al., 2008) and lacustrine (e.g. Powers et al., 2010; Pearson et al., 2011) sediments revealed that TEX_{86} correlated linearly with marine and lacustrine surface water temperatures. Consequently, it has been increasingly used for the reconstruction of past oceanic (e.g. Schouten et al., 2003; Castañeda et al., 2010) or lacustrine (e.g. Powers et al., 2005; Berke et al., 2012) temperatures. Nevertheless, its applicability to lakes was shown to be limited and sometimes biased by (i) a high input of iGDGTs produced in surrounding soils (Blaga et al., 2009) and (ii) the production of iGDGTs by types of microorganisms other

than *Thaumarchaeota* (e.g. methanogenic Archaea) thriving in the water column and/or lacustrine sediments (Blaga et al., 2009; Powers et al., 2010).

In addition to iGDGTs, Archaea also synthesize diphytanyl glycerol diethers, including archaeol (Fig. 1). Turich and Freeman (2011) compared the abundance of archaeol and caldarchaeol (GDGT I; Fig. 1) in a wide range of environments with varying salinity. They observed an increase in the ratio of archaeol to caldarcheol with increasing salinity and thus proposed the development of a paleosalinity index, the ACE (archaeol and caldarchaeol ecometric). The ACE was subsequently shown to successfully track changes in salinity in Tibetan lakes (Wang et al., 2013), but does not seem to be of use for all saline environments (Günther et al., 2014).

Another group of GDGTs, containing branched instead of isoprenoid alkyl chains (VII-IX; Fig. 1), was recently discovered in peat deposits (Sinninghe Damsté et al., 2000). Based on the structures and stereochemistry, these branched GDGTs (brGDGTs) were suggested to be produced by unknown soil bacteria (Weijers et al., 2006a), which might belong to the phylum *Acidobacteria* (Weijers et al., 2009; Sinninghe Damsté et al., 2011, 2014). They occur ubiquitously in soil (Weijers et al., 2007a; Huguet et al., 2010a) and peat (Huguet et al., 2010b, 2013; Weijers et al., 2011), as well as in lakes (Tierney et al., 2010; Pearson et al., 2011) and coastal marine sediments (Hopmans et al., 2004; Kim et al., 2007). The analysis of brGDGTs in ca. 130 surface soils distributed worldwide showed that the distributions depends primarily on air temperature and soil pH (Weijers et al., 2007a). The degree of cyclisation of brGDGTs, expressed in the cyclisation ratio of branched tetraethers (CBT), correlates rather well with soil pH. The degree of methylation of the same compounds, expressed in the methylation index of branched tetraethers (MBT), depends on mean annual air temperature (MAAT) and to a lesser extent on soil pH. The initial MBT/CBT calibration (Weijers et al., 2007a) was extended to a larger number of soils (Peterse et al., 2012). This new soil

calibration is based on the CBT and a simplified form of the MBT defined as MBT'. The MBT/CBT proxy is increasingly used to reconstruct past air temperatures, for example in deltaic and coastal regions (Weijers et al., 2007b; Donders et al., 2009), Chinese loess (Peterse et al., 2011) and lakes (Fawcett et al., 2011; Sinninghe Damsté et al., 2012a). Nevertheless, several recent studies have suggested that brGDGTs present in lakes can also originate from an in situ production in the water column or underlying sediment (e.g. Tierney and Russell, 2009; Wang et al., 2012), thereby complicating the use of the MBT/CBT proxy for lakes. This explains why several brGDGT calibrations based on lake sediments have been developed in recent years (e.g. Tierney et al., 2010; Pearson et al., 2011; Loomis et al., 2012). Based on the assumption that brGDGTs were synthesized mainly in soil, Hopmans et al. (2004) proposed another index, the BIT (branched isoprenoid tetraether) index, to track terrigenous organic matter (OM) input to aquatic settings. However, the in situ production of brGDGTs in aquatic environments and a terrestrial input of crenarchaeol questions the interpretation of BIT values (Schouten et al., 2013 and references therein).

To date, the distribution of bacterial and archaeal ether lipids in continental saline environments has been rarely investigated (Günther et al., 2014). Here, we have examined the concentration and distribution of iGDGTs, brGDGTs and archaeol in surficial sediment cores from four ponds of contrasting salinity, located in two islands from Guadeloupe (French West Indies). The two pools of GDGTs, present as either core lipids (CLs) or derived from intact polar lipids (IPLs), were analysed. IPLs (glyco- and phospholipids) contain a polar head group and are presumably derived from recently active microorganisms, whereas CLs, which are hydrolysis products of IPLs, are presumed to be of fossil origin. The aims were to (i) characterize the presence of GDGTs in ponds with contrasting salinity, (ii) test the applicability of GDGT-derived proxies (MBT'/CBT, TEX_{86} and ACE) for such sites and (iii) investigate a potential influence of salinity on GDGT-based proxies.

2. Methods

2.1.Site description and sampling

Surficial sediment cores (between 6 and 20 cm long) were collected in Guadeloupe (French West Indies) in December 2009. Four small ponds (surface area between 0.5 and 2.1 ha; Table 1) were sampled: two (La Salinette and La Grande Saline, i.e. GdeT1 and GdeT2 respectively) in Grande-Terre and two (Les Salines and La Saline, LD1 and LD2 respectively) on La Désirade Island, 10 km east of Grande-Terre (Fig. 2). The French West Indies are characterized by a wet tropical climate, with a mean annual air temperature of ca. 26 °C (France Meteorological Service, http://www.meteo.gp) and humidity ca. 75%. The average annual precipitation ranges from 1200 to 8000 mm/yr, depending on topography, with a wet rainy season from June to November and a drier season from December to May (Lloret et al., 2011). Water depth is < 1 m in the four ponds. At the time of sampling, the water of the four studied ponds exhibited a similar pH in the range 7-7.5 and slightly different temperature ranging from 27 °C to 33 °C (Table 1). Water salinity showed large differences between sites, due to their geographical location (Fig. 2). Due to their shorter distance to the ocean and flat environment, ponds from Grande-Terre are more prone to seawater input than ponds from La Désirade. They constitute slightly evaporatitic environments, inducing higher salinity than sea water (41 and 93 for GdeT1 and GdeT2, respectively; Table 1). In contrast, ponds from La Désirade Island are strongly influenced by runoff due to the topography of the island and the location of the ponds at the base of a relief, inducing low salinity of the water (4 - 8; Table 1). Water salinity and pH were determined using a multi-parameter device (WTW Multi 340i, Germany). Cores were rapidly frozen and brought back to the laboratory where they were sliced in 2-2.5 cm intervals and stored at -20 °C. Slices were then freeze dried, powdered and homogenized before total organic carbon (C_{org}) and lipid biomarker analysis.

2.2.C_{org} and lipid analysis

C_{org} content was determined at the Service Central d'Analyse du CNRS (Vernaison, France). Aliquots of the sediment samples (ca. 2-4 g) were extracted using a modified Bligh and Dyer technique, as previously detailed (Huguet et al., 2013). The extract was treated with acid-activated Cu to remove elemental S and separated over a 2 cm diameter and 10 cm height silica gel column (activated at 130 °C overnight) preconditioned with dichloromethane (DCM), using a procedure described by Huguet et al. (2013). Briefly, three fractions were prepared: F1 containing apolar lipids (70 ml DCM), F2 containing CL-GDGTs [75 ml DCM/Me_2CO (2:1, v/v) followed by 40 ml DCM/acetone (1:1, v/v) and F3 containing IPL-GDGTs [10 ml DCM/MeOH (1:1, v/v) followed by 70 ml MeOH. A small aliquot of the IPL fraction (F3) was analyzed directly using high performance liquid chromatography–atmospheric pressure chemical ionisation–mass spectrometry (HPLC-APCI–MS) to determine any carryover of CLs into the IPL fraction. The analysis showed nearly complete separation of the CL- and IPL-GDGTs. The rest of the fraction F3 was subjected to acid methanolysis (24 h at 100 °C in 1 M HCl/MeOH) to cleave off the polar head groups of IPL-GDGTs. F2 and the hydrolysed fraction F3 were then dried under N_2, ultrasonically dissolved in hexane:isopropanol (99:1, v/v) and centrifuged using an Eppendorf MiniSpin centrifuge (1 min, 7000 rpm). The supernatants were collected and analysed using HPLC-MS.

2.3.HPLC-APCI-MS

HPLC-APCI-MS was performed with an Agilent 1100 series high performance liquid chromatograph equipped with an automatic injector coupled to a PE Sciex API 3000 mass spectrometer. GDGTs were analysed using a procedure described by Huguet et al. (2013). Semi-quantification was performed by comparing the integrated signal of the respective

compound to the signal of a C_{46} synthesised internal standard (IS, Fig. 1). The analytical error for the entire extraction and analysis procedure had been previously estimated at ca. 10%.

Separate injections (10 μl) were achieved to determine the relative abundances of archaeol and caldarchaeol (GDGT I), which were analysed in single ion monitoring mode. The response factors for archaeol and caldarchaeol were assumed to be identical. Therefore, only the relative abundances of archaeol and caldarchaeol are reported.

2.4.GDGT-based indices

TEX_{86} was calculated following the equation of Schouten et al. (2002):

$$TEX_{86} = \frac{[III]+[IV]+[VI']}{[II]+[III]+[IV]+[VI']} \quad (1)$$

The Roman numbers correspond to the structures in Fig. 1. TEX_{86}-derived water surface temperature (WST) values were calculated using the calibrations of Powers et al. (2010; Eq. 2) and Kim et al. (2008; Eq. 3), developed for lacustrine and marine environments, respectively:

$$\text{WST} = 55.2 \times \text{TEX}_{86} - 14.0 \quad (2)$$

$$\text{WST} = 56.2 \times \text{TEX}_{86} - 10.78 \quad (3)$$

The MBT and CBT indices were calculated as follows (Weijers et al., 2007a):

$$MBT = \frac{[IXa + IXb + IXc]}{[VIIa + VIIb + VIIc]+[VIIIa + VIIIb + VIIIc]+[IXa + IXb + IXc]} \quad (4)$$

$$CBT = -\log\left(\frac{[VIIIb]+[IXb]}{[VIIIa]+[IXa]}\right) \quad (5)$$

The revised MBT' was calculated according to the equation proposed by Peterse et al. (2012):

$$MBT' = \frac{[IXa + IXb + IXc]}{[VIIa]+[VIIIa + VIIIb + VIIIc]+[IXa + IXb + IXc]} \quad (6)$$

Mean annual air temperature (MAAT) was estimated using the global soil calibration developed by Weijers et al. (2007a; Eq. 7) and the extended soil calibration introduced by Peterse et al. (2012; Eq. 8), respectively:

$$MAAT = \frac{MBT - 0.122 - 0.187 \times CBT}{0.020} \quad (7)$$

$$\text{MAAT} = 0.81 - 5.67 \times \text{CBT} + 31.0 \times \text{MBT'} \quad (8)$$

In some samples, GDGTs VIIIb and/or IXb were not detected and CBT could not be calculated. MAAT was therefore also estimated from MBT' and pH using the following equation (Eq. 9; Peterse et al., 2012):

$$\text{MAAT} = -23.2 + 2.86 \times \text{pH} + 33.71 \times \text{MBT'} \quad (9)$$

Several lacustrine calibrations were also used to reconstruct MAAT. These calibrations are based on lake sediments collected along a transect from the Arctic circle to the Antarctic peninsula (Pearson et al., 2011; Eq. 10) or on African sediments [Tierney et al., 2010 (Eq. 11) and Loomis et al., 2012 (Eq. 12)]:

$$\text{MAAT} = 47.4 - 53.5 \times f(VIIa) - 37.1 \times f(VIIIa) - 20.9 \times f(IXa) \quad (10)$$

$$\text{MAAT} = 50.47 - 74.18 \times f(VIIa) - 31.6 \times f(VIIIa) - 34.69 \times f(IXa) \quad (11)$$

$$\text{MAAT} = 22.77 - 33.58 \times f(VIIa) - 12.88 \times f(VIIIa) - 418.5 \times f(IXb) + 86.4 \times f(IXa) \quad (12)$$

In these equations, using the three major brGDGTs (VIIa, VIIIa and IXa), *f(i)* represents the fractional abundance of each brGDGT (*i*) defined as:

$$f(i) = \frac{[i]}{[VIIa + VIIb + VIIc] + [VIIIa + VIIIb + VIIIc] + [IXa + IXb + IXc]}$$

where *i* varies from VIIa, to VIIb, etc.

The ACE index was calculated according to the equation of Turich and Freeman (2011; Eq. 13), except that it was not multiplied by 100 in order to facilitate comparison with other indices:

$$ACE = \frac{[archaeol]}{[archaeol]+[I]} \quad (13)$$

The BIT index was calculated according to Hopmans et al. (2004; Eq. 14):

$$BIT = \frac{[VIIa]+[VIIIa]+[IXa]}{[VI]+[VIIa]+[VIIIa]+[IXa]} \quad (14)$$

The standard deviation (based on duplicate analyses) for TEX_{86}, MBT/MBT', CBT, BIT and ACE indices was 0.005, 0.005, 0.02, 0.006 and 0.004, respectively.

3. Results

3.1.Occurrence of GDGTs

HPLC-MS revealed the presence of iGDGTs and brGDGTs in all the CL and IPL fractions, although the relative abundance of the different GDGTs varied between the four ponds (Fig. 3). Caldarchaeol (GDGT I) was predominant among iGDGTs in both CL and IPL fractions from Grande-Terre, representing more than ca 60% of total iGDGTs (Fig. 3). In contrast, crenarchaeol (GDGT VI) was more abundant than GDGT I in CL fractions of samples from La Désirade, but appeared as abundant as GDGT I (Fig. 3) in the IPL fractions of these samples.

Regarding brGDGTs, GDGT VIIa was as abundant as the less methylated GDGTs VIIIa and IXa in CL and IPL fractions from Grande-Terre, each representing about 20 - 40% of total brGDGTs (Fig. 3). In contrast, in ponds from La Désirade, GDGT VIIa was present in much lower abundance (< 10% of total brGDGTs in both CL and IPL pools of most samples) than GDGTs VIIIa and IXa. In three of the four ponds (LD1, GdeT1 and GdeT2), brGDGTs containing one (VIIIb and IXb) and two (VIIIc and IXc) cyclopentyl moieties were much less abundant than the corresponding acyclic GDGTs (VIIIa and IXa) and were even not detected in some samples. In contrast to the other sites, GDGT IXb was as abundant as GDGT VIIIa in pond LD2, representing ca. 20 – 30% of total brGDGTs (Fig. 3). It should be noted that cyclic

GDGTs VIIb and VIIc were not detected in any sample, implying that MBT and MBT' values were identical.

3.2.Variation in GDGT abundance and distribution with depth

The concentrations of the individual iGDGTs and brGDGTs normalised to C_{org} showed comparable patterns downcore (Supplementary Fig. 1). Therefore, only downcore trends in total iGDGT and total brGDGT concentrations (Fig. 4) are discussed in this section. For each pond, iGDGT and brGDGT concentrations generally show similar depth profiles. Nevertheless, the variation in concentration with depth was strongly dependent on the water pond. In LD1, the concentrations of CL iGDGTs and brGDGTs showed a decrease from the surface to the bottom of the core, whereas an opposite trend was observed for GdeT2. For LD2, iGDGT and brGDGT concentrations were low in the surface layer, reached a maximum between 2.5 and 5 cm depth, and increased slightly below 7 cm. In GdeT1, GDGT concentration decreased by a factor 2 between 2 and 8 cm depth, and was maximal between 10 and 16 cm.

GDGT concentration in CL and IPL pools generally showed similar downcore trends, except in GdeT2, where the abundance of IPL GDGTs reached a minimum between 8 and 10 cm depth, which was not visible in the CL pool (Fig. 4). Nevertheless, the relative proportion of CL GDGTs with respect to total (i.e. CL + IPL) GDGTs varied with depth at most sites. For example, for GdeT2, the relative abundance of iGDGT CLs vs. total iGDGTs increased downcore, from ca. 25% to ca. 63%.

In the LD2, GdeT1 and GdeT2 ponds, no major change in brGDGT distribution was observed with depth, as shown by the generally low variability in MBT' values along the cores (Fig. 4). In contrast, the distribution of brGDGTs showed downcore variability in LD1 pond, as reflected in the variation in MBT' values between 0 and 6 cm depth (Fig. 4).

The distribution of iGDGTs varied with depth in LD2, GdeT1 and GdeT2, inducing a high variability in TEX_{86} values in these ponds (Fig. 4). In LD1, iGDGTs II and IV, involved in the calculation of the TEX_{86}, were not detected in the CL fractions until 4 cm depth. Comparable TEX_{86} values were nevertheless obtained from the three IPL fractions (Fig. 4).

3.3.Comparison of GDGT-derived parameters from the four ponds

BIT, TEX_{86}, MBT' and CBT mean values for Grande-Terre ponds were generally different from those of La Désirade ponds. For CL GDGTs, the BIT and CBT mean values were generally higher in Grande-Terre ponds (Supplementary Tables 1 and 2), whereas the mean MBT' and TEX_{86} mean values were higher in ponds from La Désirade. With a few exceptions, the BIT, TEX_{86}, MBT' and CBT mean values calculated from the entire cores were similar in the two lipid pools (CLs and IPLs; Supplementary Tables 1 and 2).

3.4.Archaeol and caldarchaeol distributions

The ACE index, based on the relative abundances of caldarchaeol (GDGT I) and archaeol, was determined for the CL and IPLs fractions of the four ponds (Fig. 5; Supplementary Table 2). It had similar values for all ponds (mean between 0.94 and 0.98 for the CL pool; Fig. 6) and there were no obvious differences in the values between the CL and IPL pools, except for GdeT1 (0.94 ± 0.06 and 0.87 ± 0.10 for CLs and IPLs, respectively). The relative abundance of caldarchaeol vs. total iGDGTs varied between the four ponds, increasing from ca. 20-30% for the CL pools of La Désirade to ca. 60-80% for Grande-Terre ponds (Fig. 5). A similar increase in the relative abundance of caldarchaeol with salinity was observed for IPLs.

4. Discussion

4.1.Sources of iGDGTs in La Désirade and Grande-Terre ponds

Caldarchaeol (GDGT I) is suggested to be produced by all major groups of Archaea, except halophilic Archaea, whereas crenarchaeol (GDGT VI) is hypothesized to be essentially produced by NH_4^+ oxidizing *Thaumarchaeota* (Schouten et al., 2013 and references therein). As for iGDGTs II, III and IV, they are produced mainly by three phyla within the domain of Archaea, namely: *Thaumarchaeota*, *Crenarchaeota* and *Euryarchaeota* (Pearson and Ingalls, 2013 and references therein). For ponds from La Désirade, the iGDGT distribution resembles that described for mixed marine archaeal communities (e.g. Sinninghe Damsté et al., 2002; Wuchter et al., 2005; Lipp and Hinrichs, 2009). The high relative abundances of GDGTs I and VI and the low relative abundances of GDGTs II, III and IV (Fig. 3) suggest a mixed source (*Thaumarchaeota, Crenarchaeota and Euryarchaeota*) for iGDGTs in these two poorly saline ponds.

In contrast, GDGT I is largely predominant among iGDGTs in Grande-Terre ponds (Fig. 3). The differences in iGDGT sources between the four ponds can be deciphered by calculating the ratio of GDGT I to GDGT VI, developed to assess the contribution of iGDGTs produced by methanogenic Archaea in lacustrine environments (Blaga et al., 2009). Cultures enriched in *Thaumarchaeota* exhibit a GDGT I/GDGT VI ratio always < 2, whereas methanogenic Archaea produce GDGT I but no GDGT VI. The ratio GDGT I/GDGT VI is lower than 1 in most samples from La Désirade, whereas values 3 to 6 times and 10 to 41 times higher occur in the CL and IPL fractions of Grande-Terre sediments, respectively (Supplementary Table 2). This strongly suggests a substantial contribution of methanogenic Archaea to iGDGTs in Grande-Terre ponds, in contrast to La Désirade ponds.

The CL and IPL pools of iGDGTs seem to be closely related in LD1, LD2 and GdeT1 ponds, as shown by the similar downcore variation in CL and IPL iGDGT concentrations (Fig. 4). This indicates that CL GDGTs are likely derived from IPL GDGTs, although distinct functional head groups (phospho- vs. glycosyl-) may have different degradation kinetics

which may sometimes lead to differences in distribution between the CL and IPL pools (Schouten et al., 2010). The quantitative connection between the CL and IPL pools in most of the ponds might further indicate that the production of IPL iGDGTs by planktonic/benthic Archaea, the subsequent hydrolysis of their polar head groups and the preservation/degradation of the resulting CL GDGTs are closely related processes. In contrast, in GdeT2, the depth profiles of IPL and CL iGDGTs show different trends, likely reflecting the decoupling of IPL production and IPL degradation/CL preservation.

The downcore trends in iGDGT concentration strongly differ between the different water ponds, depending on the relative importance and kinetics of iGDGT production in the water column/sediment and subsequent preservation within the sediments. Thus, the downcore decrease in CL and IPL iGDGTs concentrations in LD1 (Fig. 4) could result from a lower production of iGDGTs in the water column/sediment at the time of deposition, even though the hypothesis of a concomitant degradation of iGDGTs with depth cannot be totally excluded. In contrast, iGDGT profiles for LD2 and GdeT1 show significant peaks at 2.5-5 cm and 14-16 cm depth, respectively (Fig. 4). The high relative abundance of IPL vs. CL iGDGTs (> 50%) at these two depths suggests either a substantial in situ production of these compounds by benthic Archaea, or an increased production of iGDGT IPLs in the water column followed by their preservation in the sediment.

The abundance of crenarchaeol regio isomer (GDGT VI') relative to both isomers (VI + VI') is unusually high in the four ponds, both in the CL (> 10% in most samples) and the IPL (> 20%) pools. This compound has been reported in very low abundance (< 5%) in enrichment cultures of Group 1.1a aquatic *Thaumarchaeota* (Pitcher et al., 2011) as well as in European (Blaga et al., 2009) and Tibetan (Wang et al., 2012) lacustrine sediments. In contrast, it has been observed to be much more abundant in Group 1.1b *Thaumarchaeota* enriched from soils (ca. 21%; Sinninghe Damsté et al., 2012b) as well as in Tibetan (Wang et

al., 2012; Liu et al., 2013) or African (Sinninghe Damsté et al., 2012a; Coffinet et al., 2014) soils, where its abundance is between 5 and 15%. In the present case, it seems unlikely that the high relative abundance of GDGT VI' is due to a strong input of soil *Thaumarchaeota* and only a small contribution from aquatic *Thaumarchaeota*, both in Grande-Terre and La Désirade sediments. Indeed, it is essentially present in the IPL fraction, which is considered as deriving from recently active Archaea. We thus hypothesize that the crenarchaeol regio isomer (GDGT VI') in the four ponds is produced mainly by some yet uncharacterized *Thaumarchaeota*, possibly belonging to Group 1.1b. This would be in good agreement with the observation of a high abundance of this GDGT in tropical marine waters and sediments (e.g. Wuchter et al., 2005; Kim et al., 2008; Pitcher et al., 2010) and with the presence of sequences of Group 1.1b *Thaumarchaeota* in some marine sediments (e.g. Park et al., 2008). It should be noted that crenarchaeol has been rarely reported from hypersaline environments such as GdeT2 pond. It has been detected in surface sediments from the Red Sea, where it was suggested to be biosynthesized by a specific population of *Thaumarchaeota* adapted to the high temperature and high salinity of this environment (Trommer et al., 2009).

4.2.Sources of brGDGTs in La Désirade and Grande-Terre ponds

BrGDGTs in aquatic environments can have two main sources. First, they can be eroded from catchment soils where they are produced (Weijers et al., 2007a) and be transported by rivers and run-off (e.g. Niemann et al., 2012; Günther et al., 2014). An increasing number of studies has shown, however, that brGDGTs can also be produced in situ, i.e. in the water column and/or within the sediment (e.g. Tierney and Russell, 2009; De Jonge et al., 2014). Depending on the aquatic system, brGDGTs can thus derive from either source, but more likely originate from both (e.g. Tierney et al., 2012; Naeher et al., 2014). This consequently complicates the application of brGDGT-based proxies such as MBT/CBT to aquatic systems.

The comparison of brGDGT distribution and concentration between sediments from Grande-Terre and La Désirade ponds and surrounding soils could have unambiguously helped determine the brGDGT source(s) in these ponds. Unfortunately, no watershed soil sample was available for such a study. However, the high abundance of IPL relative to total (CL + IPL) brGDGTs in all the ponds (between 20 and 70%; Fig. 4) suggests that a significant part of brGDGTs originates from in situ production. The proportion of IPL brGDGTs in soils is indeed generally much lower (ca. 5-25%; e.g. Peterse et al., 2010; Buckles et al., 2014a) than in most of our sediments (30-65%), implying that all the IPL brGDGTs detected in Grande-Terre and La Désirade ponds cannot be exclusively soil-derived. The relative abundance of IPL brGDGTs vs. CLs is especially higher in Grande Terre (ca. 50-65%) than in La Désirade ponds (< 40%), suggesting a larger contribution of in situ production vs. soil-derived brGDGTs in the former.

Grande-Terre and La Désirade water ponds are also characterised by significant differences in brGDGT distributions, in both IPL and CL pools (Fig. 3). The relative abundance of GDGT VIIa is much lower in La Désirade sediments (< 10% of total brGDGTs) than in those from Grande-Terre (ca. 30-35%; Fig. 3). Several studies of tropical (e.g. Tierney et al., 2009; Loomis et al., 2011; Das et al., 2012) and temperate (e.g. Tierney et al., 2012; Loomis et al., 2014) lakes have reported differences in brGDGT distribution between soils and adjacent lake sediments. They suggested that an increase in the abundance of the most methylated brGDGTs (GDGTs VII) may indicate in situ production of brGDGTs within the lacustrine water column (and/or sediment). Therefore, the higher relative abundance of GDGT VIIa in Grande-Terre vs. La Désirade further supports a significant in situ production of brGDGTs in the former ponds.

Lastly, unlike ponds from Grande-Terre, ponds from La Désirade are strongly influenced by runoff due to the topography of the island. Therefore, topographical considerations, combined

with brGDGT distributions and IPL brGDGTs relative abundances, suggest that the proportion of soil-derived vs. in situ-produced brGDGTs is much higher in La Désirade than in Grande-Terre ponds. It thus seems likely that brGDGTs are produced predominantly in situ in Grande-Terre ponds, especially La Salinette (GdeT1), whereas in La Désirade ponds, brGDGTs likely result from a mixture of soil and aquatic sources.

As previously above for iGDGTs, the downcore trends in brGDGT concentration showed large differences between the four water ponds (Fig. 4), which may notably be explained by variation in (i) the relative importance of soil input vs. in situ production and, (ii) the accumulation and preservation potential of brGDGTs derived from these two sources in each pond. Additional studies are needed to decipher the differences in preservation of soil-derived and in situ-produced brGDGTs in sediments. Independently of this, depth profiles of brGDGTs and iGDGTs were observed to be mainly similar in each water pond, for both CL and IPL pools (Fig. 4). Similarly, iGDGT and brGDGT concentrations have been shown to co-vary along a 4.4 m sediment core from the southern Yellow Sea of China (Ge et al., 2014), and co-variation of brGDGT and crenarchaeol concentrations was also observed in marine and lacustrine environments (Fietz et al., 2011; Grauel et al., 2013). The concentrations in iGDGTs and brGDGTs in sediments are controlled by specific production, transport, deposition and preservation processes. Nevertheless, as suggested by Ge et al. (2014), the co-variation in iGDGT and brGDGT concentrations may indicate a common environmental process, e.g. co-variance between riverine nutrient input and marine/lacustrine productivity. A similar explanation may hold for the co-variance of iGDGT and brGDGT concentrations in the present ponds. It is also possible that brGDGT-producing Bacteria have a similar ecological niche to Archaea, which would explain such co-variation in lipid profiles. The same hypothesis was formulated by Tierney et al. (2010) to explain the correlation between the concentrations of crenarchaeol and brGDGTs with two cyclopentyl rings in African lakes.

Loomis et al. (2014) however recently dismissed this idea based on the fact that (i) brGDGT concentrations and distributions were not correlated with N in East African water column/sediments and (ii) *Thaumarchaeota* are ammonia-oxidising Archaea. Therefore, the hypothesis of an ecological relationship between Archaea and brGDGT-producing Bacteria will remain speculative until the exact brGDGT producers and the metabolic properties of these microorganisms are determined.

4.3.Implications for GDGT-based environmental proxies

4.3.1. ACE index

Although the four ponds investigated are characterized by contrasting salinity values between 4 and 91 (Table 1), comparable ACE values (between ca. 0.9 and 1; Fig. 5) occur for all the ponds whatever the GDGT fraction (CL or IPL). A systematic higher concentration of archaeol relative to caldarchaeol (> 90 %) is present even for La Désirade ponds characterized by low salinity (<10). Such high values of the ratio were expected more for the hypersaline ponds of Grande-Terre, since the production of caldarchaeol was reported to be minimal in hypersaline environments (Turich and Freeman, 2011).

The fact that the ACE index does not systematically reflect changes in salinity has already been cautioned by Günther et al. (2014) in a study of saline Tibetan lakes. The authors further suggested that the ACE index might better represent changes in archaeal communities occurring in environments with contrasting salinity. The comparison of the iGDGT distribution in the present four ponds may indicate a transition from a mixed archaeal community (*Thaumarchaeota*, *Crenarchaeota* and *Euryarchaeota*) in the least saline ponds of La Désirade, to a community dominated by methanogenic Archaea (*Euryarchaeota*) in Grande-Terre ponds. This transition is reflected in the relative abundance of caldarchaeol vs. total iGDGTs, which increases with salinity whatever the GDGT pool (Fig. 5). The strong

proportion of caldarchaeol in the most saline ponds from Grande Terre strongly supports a production of this GDGT by (hyper)halophilic archaea, although these microorganisms are generally believed to produce only archaeol (Teixidor et al., 1993; Kates et al., 1996; Grice et al., 1998). The presence of caldarchaeol in cultures of halophilic Archaea has never been reported, but there are indications that biphytane carbon chains can be biosynthesized by such microorganisms (Turich et Freeman, 2011 and references therein). Additional studies are clearly needed to better constrain the sources of caldarchaeol in various haline environments before the ACE can be confidently applied as a salinity proxy.

4.3.2. BIT index

The BIT index was initially developed as an indicator of the relative input of soil-derived vs. marine organic matter in marine settings (Hopmans et al., 2004). It is also used in lacustrine environments to estimate the input of soil OM (e.g. Blaga et al., 2009). Its application can be complicated by (i) high input of soil-derived crenarchaeol and (ii) in situ production of brGDGTs in the aquatic environment (Schouten et al., 2013 and references therein). In the present case, the BIT index based on the CL fraction is roughly higher than 0.8 in three of the four ponds (LD1, GdeT1 and GdeT2) and higher than 0.6 in the last one (LD2; Fig. 4). These high BIT values cannot result only from an important input of soil OM to the ponds, but also reflect a substantial in situ production of brGDGTs, especially in Grande-Terre ponds as discussed above. Lacustrine brGDGT production has already been observed to lead to high BIT index values for several lakes, such as lake Lugano (Bechtel et al., 2010), Lucerne (Blaga et al., 2011), Challa (Sinninghe Damsté et al., 2009; Buckles et al., 2014b), Tanganyika (Schouten et al., 2012), Superior (Woltering et al., 2012) or Loch Lomond (Buckles et al., 2014a). The BIT values are lower for the ponds of La Désirade than for those of Grande-Terre (Fig. 4), which is likely due to (i) the lower abundance of crenarchaeol (both absolute and

relative to total brGDGTs) and (ii) the potentially higher proportion of brGDGTs derived from in situ production in Grande-Terre ponds. These results warrant caution when applying and interpreting the BIT values from saline ponds, where the reliability of the index depends on the aquatic system considered and on the importance of autochthonous vs. allochthonous production of brGDGTs and crenarchaeol.

4.3.3. TEX_{86}

Proper application of TEX_{86} requires that *Thaumarchaeota* living in the water column are the predominant source of iGDGTs in the underlying sediments. A strong input of soil-derived iGDGTs to lakes can indeed modify the signal from iGDGTs produced in situ by *Thaumarchaeota*, leading to biased TEX_{86} values and TEX_{86}-derived temperature values. Blaga et al. (2009) suggested that TEX_{86} could only be applied to lacustrine environments where the BIT was < 0.4 although, in some lakes, TEX_{86} may still be applied as a temperature proxy despite high BIT values (Buckles et al., 2014a). The substantial contribution of methanogenic archaea to iGDGTs in Grande-Terre ponds, supported by high values of GDGT I/GDGT VI (see above), would suggest that TEX_{86} values calculated for these sediments are probably not reliable for temperature reconstruction. This was indeed verified by estimating WST from TEX_{86} values using the calibrations developed for lacustrine sediments by Powers et al. (2010; Eq. 2) and for marine sediments by Kim et al. (2008; Eq. 3). The latter calibration was used since Grande-Terre water ponds show comparable or higher salinity than that observed in marine environments. TEX_{86}-derived WST estimates were compared with WST measured during sampling (27-33 °C; Table 1) and with MAAT recorded in the region (ca. 26 °C). Whatever the calibration used, temperature estimates derived from Grande-Terre ponds are much lower (by up to 20 °C) than expected MAAT or measured WST (Fig. 6). In contrast, in La Désirade ponds, TEX_{86}-derived temperature values generated with either the lake

calibration of Powers et al. (2010) or the marine calibration of Kim et al. (2008) are in relative agreement (although slightly higher) than the single point measurements of WST (Table 1) and the expected MAAT (Fig. 6), taking into account the calibration error in both calibrations (± 3.6 °C and ± 1.7 °C, respectively). The lacustrine calibration by Powers et al. (2010) was developed mainly from medium and large lakes, where in situ produced crenarchaeol is sufficiently abundant to provide valuable TEX_{86} values, in contrast with most of the small lakes. The present results indicate that TEX_{86} can also be suitable for local water temperature reconstruction in small ponds such as those of La Désirade, when (i) iGDGT production by methanogenic Archaea is not predominant and (ii) crenarchaeol is present at sufficient concentration to produce reliable TEX_{86} values. Whatever the calibration used, TEX_{86}-derived temperature for the CL and IPL pools differs by only ca. 2-3 °C in most ponds (Fig. 6), suggesting that both lipid fractions can be differently used to reconstruct WST.

4.3.4. MBT/CBT

Several calibrations based on soil or lacustrine data were used to reconstruct brGDGT-derived MAAT for the four ponds (Fig. 6). Similar MAAT values were generally obtained using CL or IPL brGDGTs supporting the idea that, for all the ponds, brGDGTs in the two lipid pools have the same origin. The application of the original soil calibration of Weijers et al. (2007a) to CL brGDGTs in La Désirade sediments yielded slightly lower temperature estimates than the recorded MAAT (Fig. 6). Nevertheless, these values can be considered as fairly reliable when considering the relatively large standard error associated with the calibration (± 5 °C). In contrast, MAAT estimates obtained using the revised soil calibration of Peterse et al. (2012) were lower (by 6 to 8 °C) than expected MAAT, and outside the calibration error. It should be noted that CBT could not be calculated for some of the samples.

Therefore, MAAT was also calculated from MBT' and pH using Eq. 8 developed by Peterse et al. (2012), but this did not significantly improve MAAT reconstruction (Fig. 6).

Lacustrine MBT/CBT calibrations have also been developed to take into account the in situ production of brGDGTs in the water column and/or sediment, which generally leads to an underestimation of observed MAAT (e.g. Tierney and Russell, 2009; Tierney et al., 2010). Here, MAAT values were reconstructed using two regional lake calibrations covering equatorial Africa (Tierney et al., 2010; Loomis et al., 2012), and with a more global calibration developed by Pearson et al. (2011). The latter was established on the basis of mean summer air temperature (rather than MAAT) from lakes distributed from the Scandinavian Arctic to the Antarctic. It is noteworthy that the air temperature in the French Western Indies region exhibits low seasonal variability (26.4 ± 1.2 °C; data from France Meteorological Service, http://www.meteo.gp), which is lower than the root mean squared error (RMSE) of each of the three calibrations considered (ranging from 1.9 and 2.2 °C). Therefore, the temperature values reconstructed from the Pearson et al. (2011) calibration can be considered as equivalent to MAAT. The three lake calibrations applied to the CL fraction and IPL fraction from La Désirade sediments yielded higher or lower MAAT values than expected (from ca. 4 to 14 °C; Fig. 6). Overall, the application of the Weijers et al. (2007a) soil calibration to La Désirade sediments generally yields better temperature estimates than lacustrine calibrations which provide overestimated temperature values. This further supports a predominant soil origin for brGDGTs in La Désirade ponds.

MAAT estimates from Grande-Terre ponds generated using either soil or lacustrine calibrations are systematically much lower (by 11 to 21 °C) than recorded regional MAAT (Fig. 6). This shows that both types of calibration are unadapted to temperature reconstruction in Grande-Terre ponds. An offset between estimated temperature and measured temperature may be observed for lakes where the relative contributions of soil-derived and in situ-

produced brGDGTs largely differ from those in the lakes included in the calibration set. As discussed above, a large part of brGDGTs in Grande-Terre sediments is likely derived from in situ production. This likely explains the large mismatch between estimated and expected temperatures at these sites. The offset might also be due to differences between bacterial communities biosynthesizing brGDGTs in Grande-Terre ponds and in most of the lakes investigated so far. Grande-Terre ponds are characterized by high salinity (> 40; Table 1), where specific halophilic microbial communities likely produce a specific distribution of brGDGTs. Consequently, the relationship between air temperature and brGDGT distribution at such sites may differ from those observed previously in the marine realm and lakes. The production of brGDGTs in different types of saline and hypersaline environments clearly needs to be further investigated.

5. Conclusions

The abundance and distribution of brGDGTs, iGDGTs and archaeol in four tropical water ponds of contrasting salinity located in two islands from the French Western Indies, Grande-Terre and La Désirade were examined. Distinctive GDGT distributions between the two sites have major implications in terms of application of GDGT-based proxies that can be summarized as follows:

- Despite the much higher salinity of Grande-Terre ponds, the relative abundance of archaeol vs. caldarchaeol (ACE index) was constant in all ponds, implying that the sources of caldarchaeol in saline environments need to be better constrained before the ACE index can be confidently applied as a salinity proxy.

- A substantial contribution of caldarchaeol (GDGT I) from methanogenic Archaea was evidenced in the most saline ponds from Grande-Terre, preventing the application of TEX_{86} as a temperature proxy. In contrast, both caldarchaeol and crenarchaeol were present in high relative abundances in La Désirade ponds, where the TEX_{86} appeared a suitable proxy for local temperature reconstruction.
- Based on the relative proportions of CLs and IPLs, lipid distributions and topographical considerations, brGDGTs are suggested to be predominantly produced in situ in Grande-Terre ponds, whereas they likely result from a mixture of soil and aquatic sources in La Désirade.
- The differences in brGDGT sources between the two islands are reflected in the temperature estimates based on these compounds and most of the available lacustrine or soil calibrations. The soil calibration of Weijers et al. (2007a) yielded the best temperature estimates for the least saline La Désirade ponds, whereas temperature reconstructed for the most saline Grande-Terre ponds was systematically lower than expected.
- The higher proprotion of in situ-produced vs. soil-derived brGDGTs in Grande-Terre ponds, combined with the presence of halophilic microbial communities biosynthesizing specific brGDGT distribution, might explain the offset between expected and estimated temperatures in these (hyper)saline ponds.

Overall, our work shows that the sources of brGDGTs, iGDGTs and archaeol may strongly differ in aquatic environments with varying salinity even at a regional scale, so caution is warranted before tetraether-based environmental proxies can be applied to such settings.

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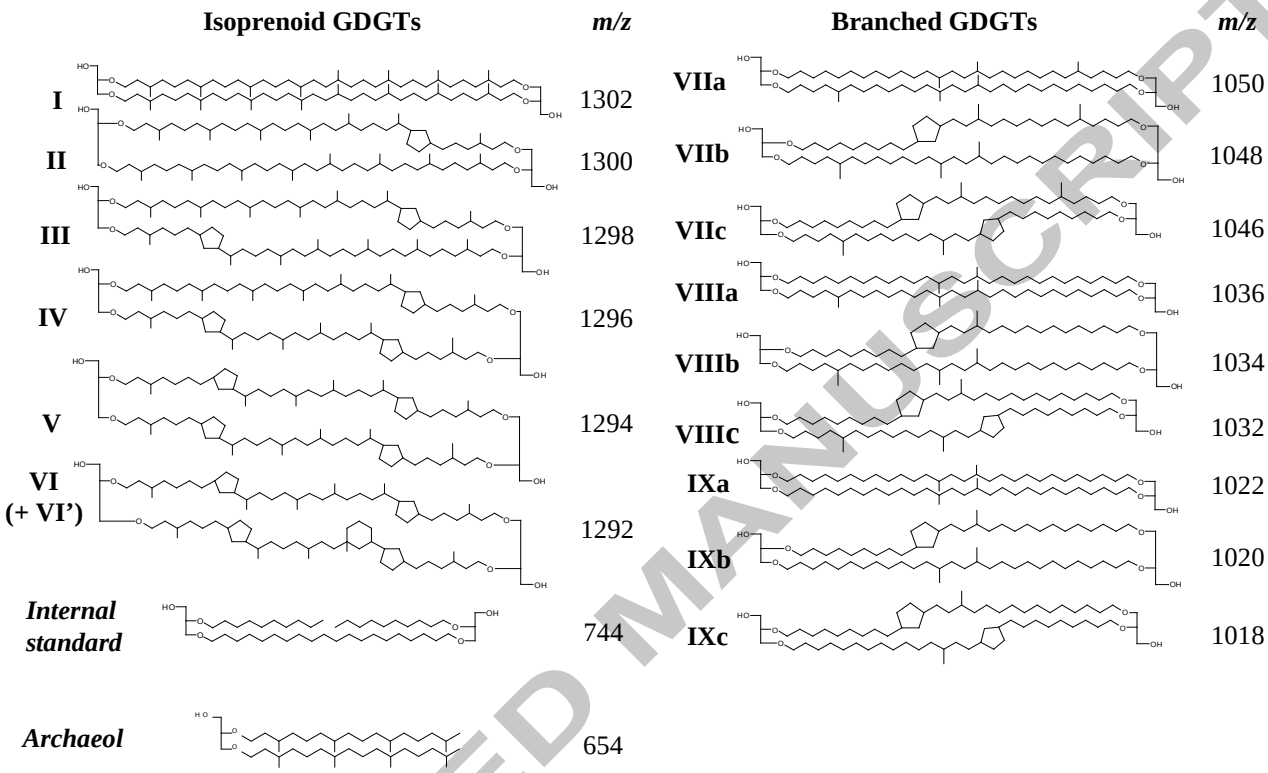

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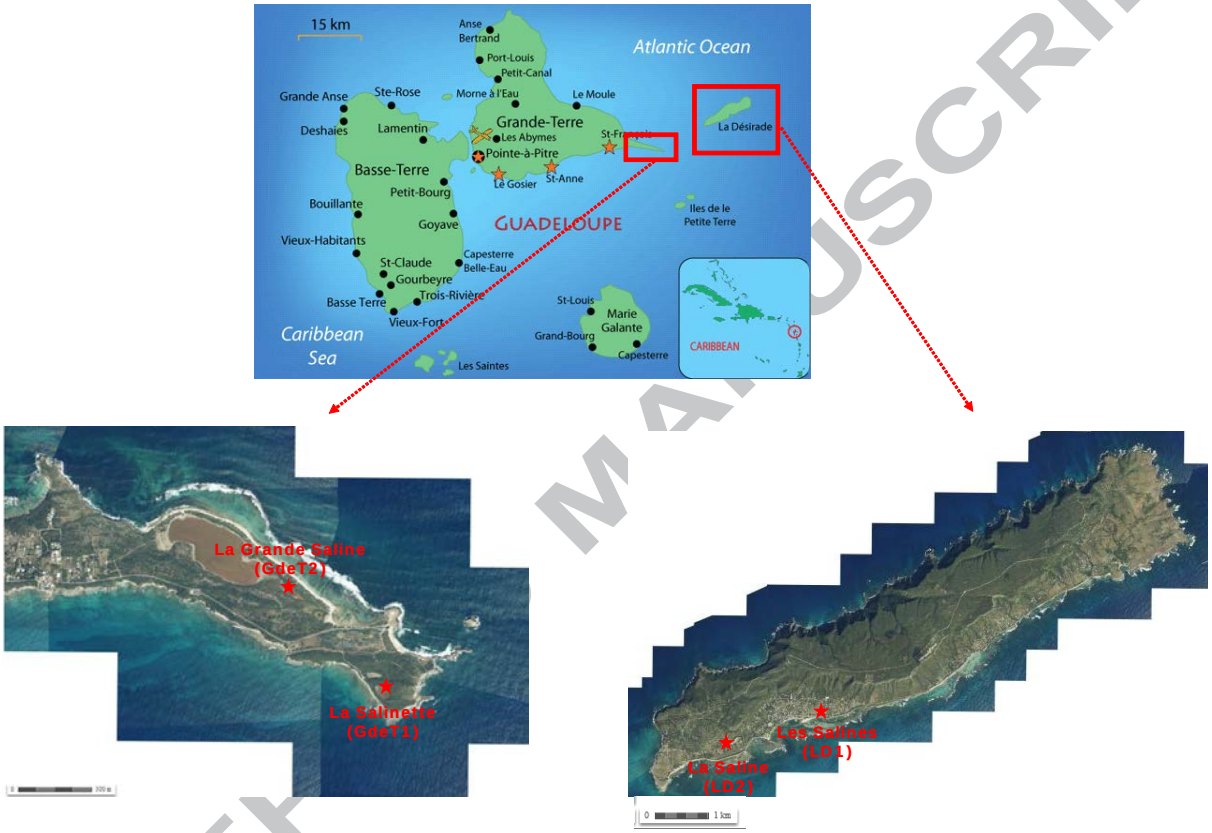
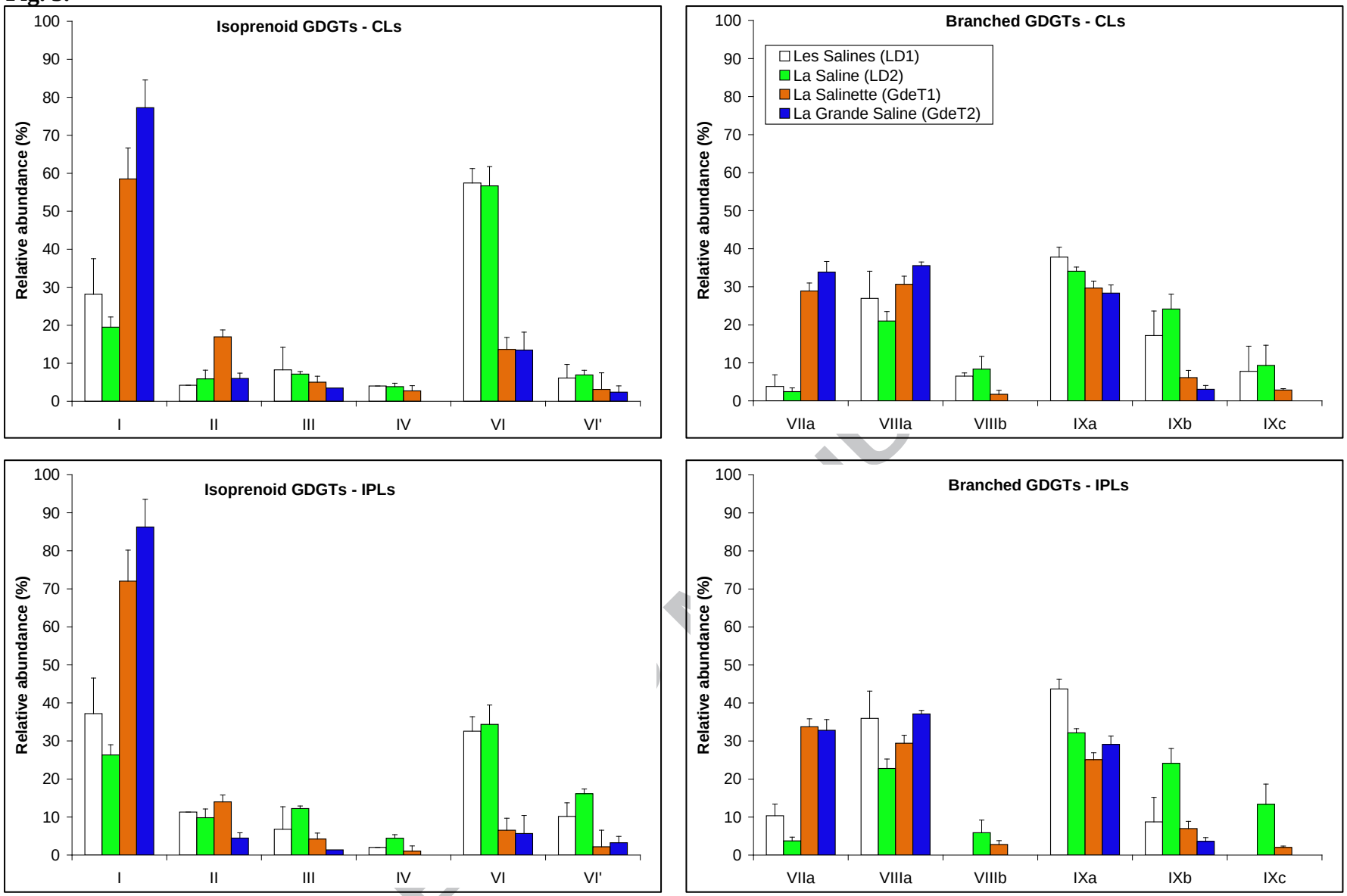


Grande-Terre (Pointe des Châteaux) **La Désirade**

Fig. 2.

Fig. 3.



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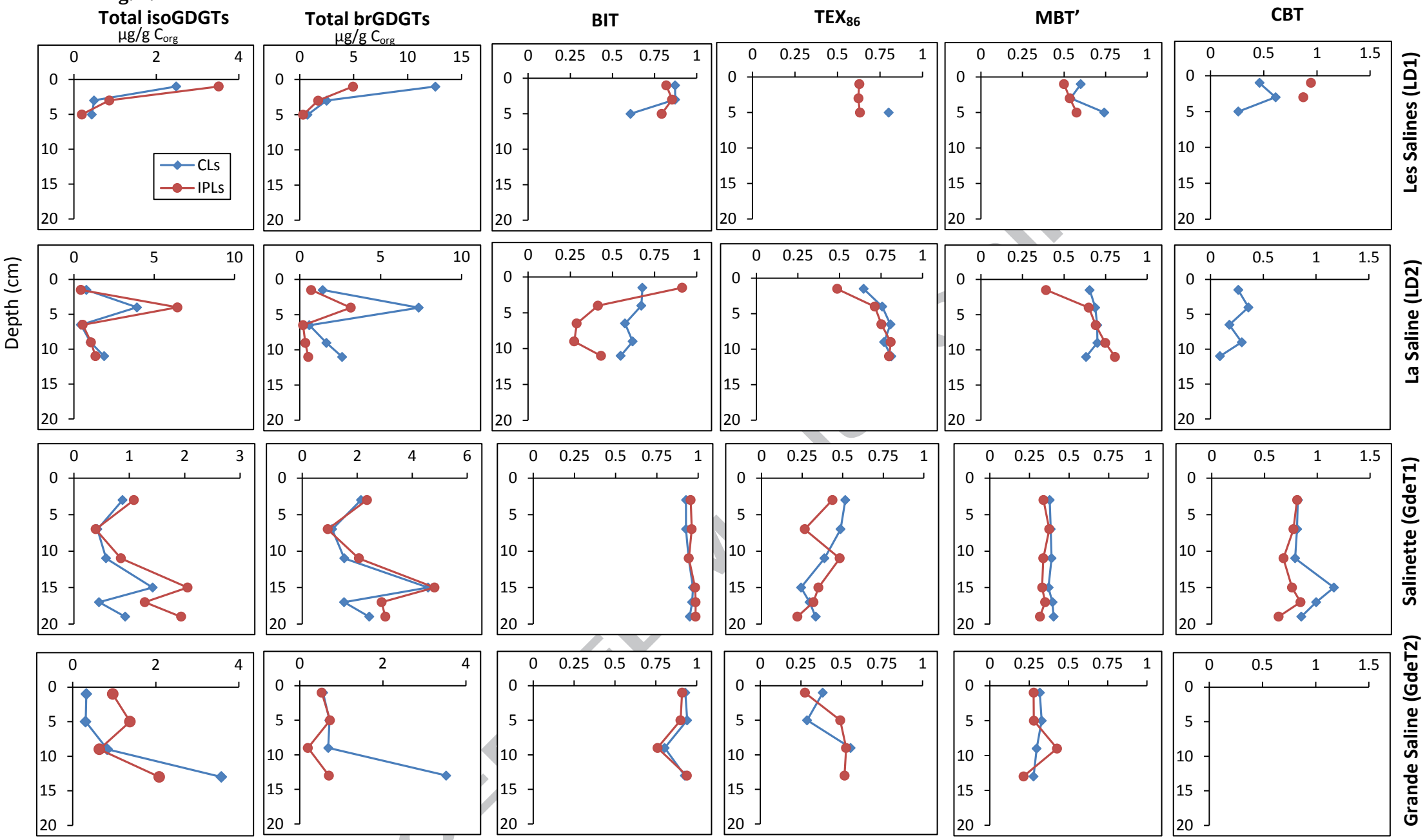


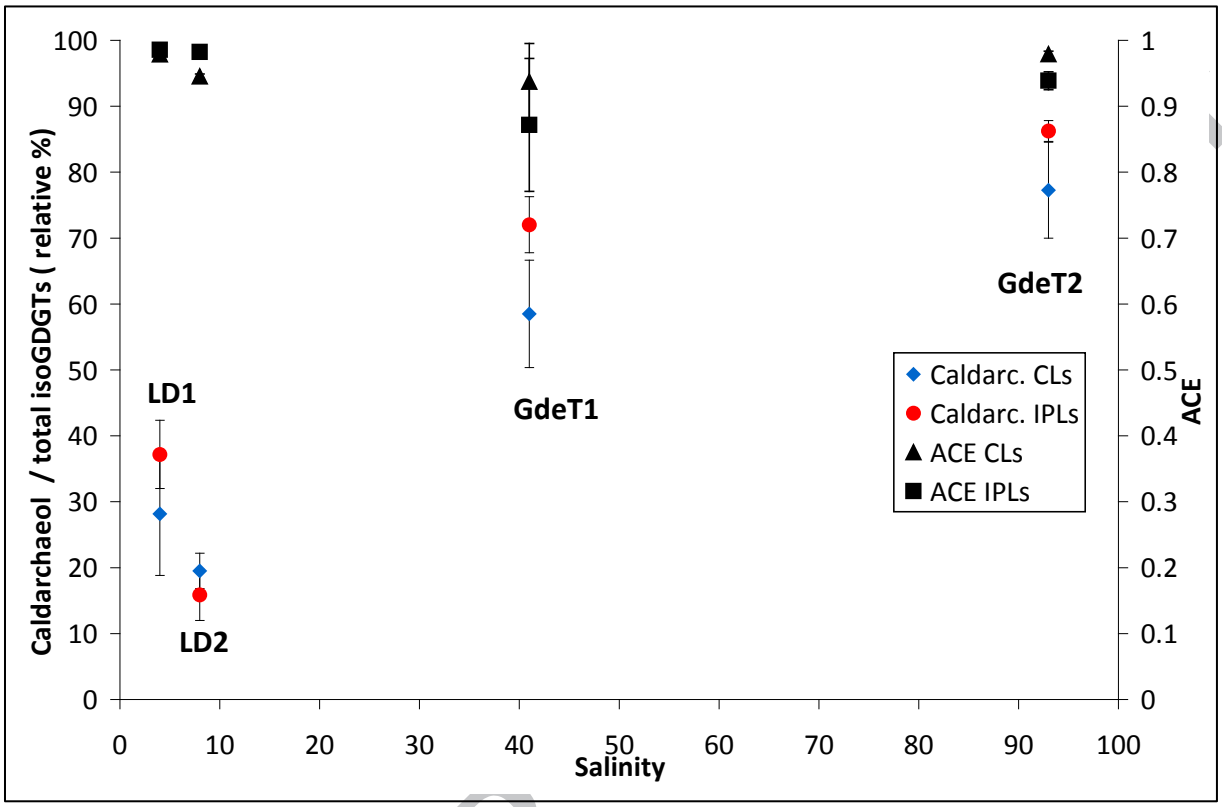
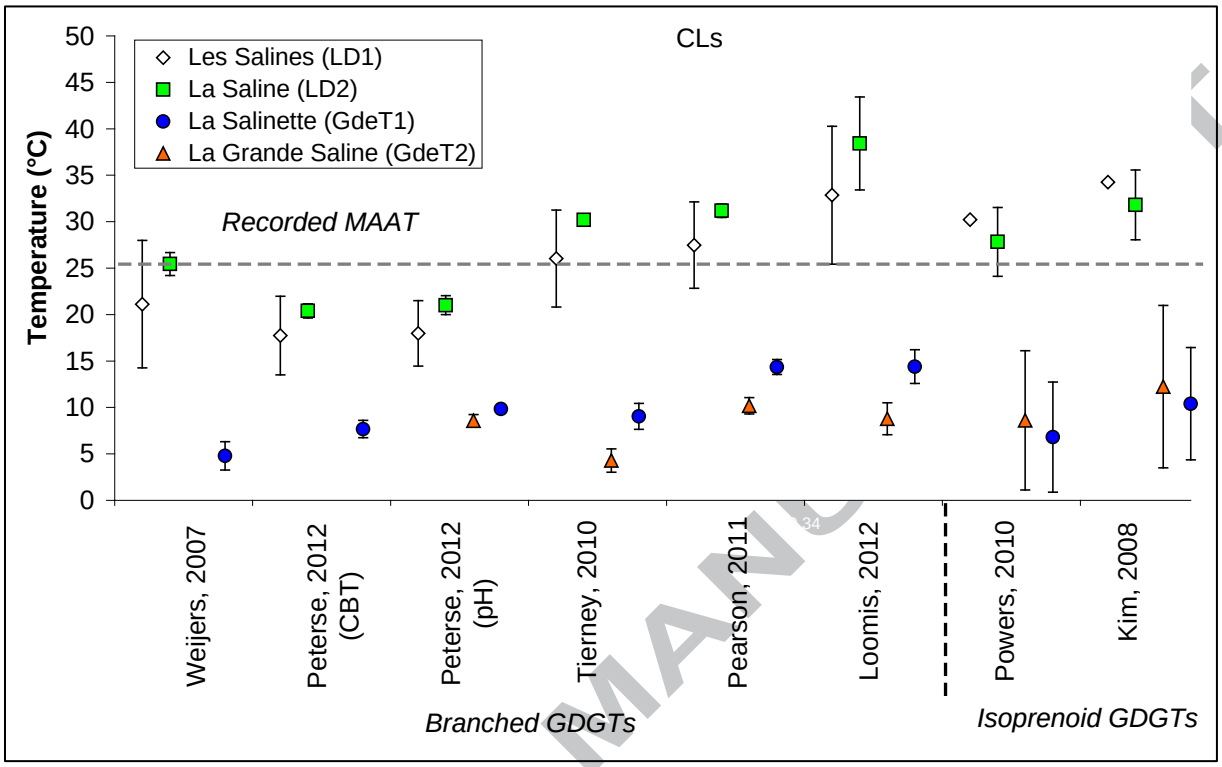


Fig. 5.

(a)



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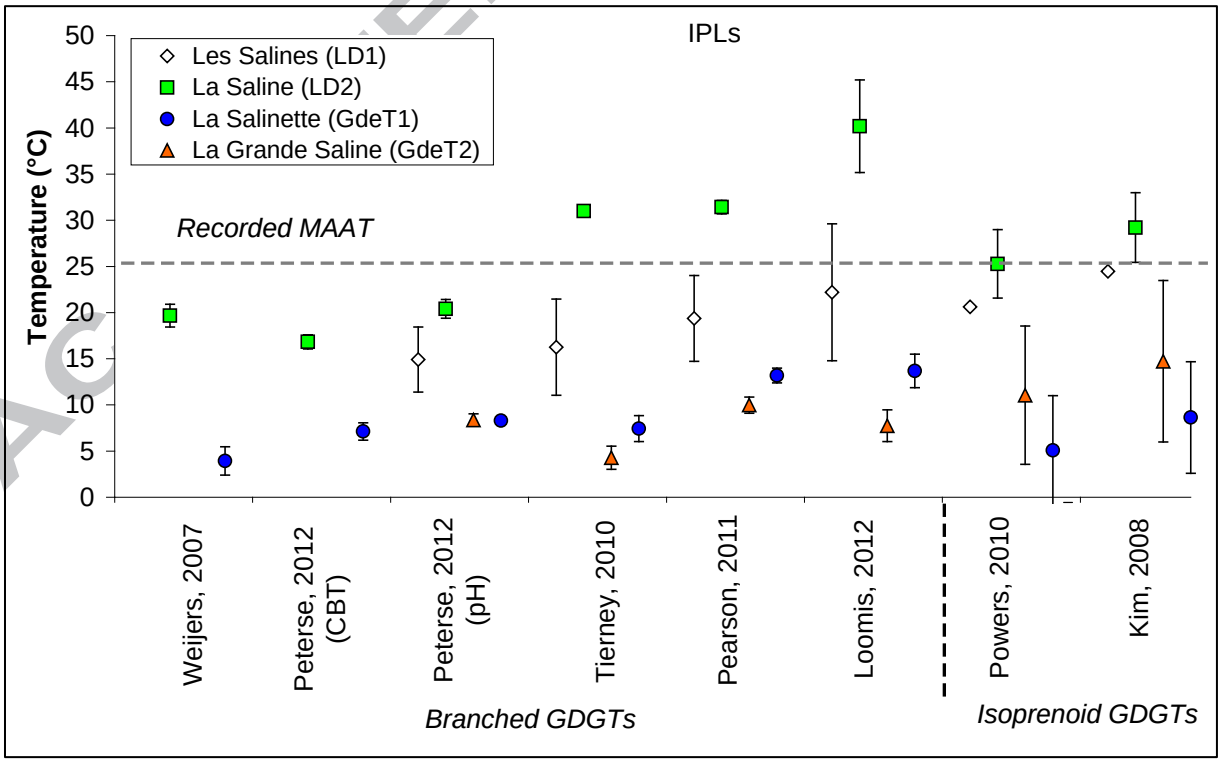

Fig. 6.

Fig. 1. Structures of isoprenoid and branched glycerol dialkyl glycerol tetraether (GDGT) core lipids, archaeol and internal standard (IS).

Fig. 2. Location of the four ponds investigated in the French Western Indies. Two [La Salinette (GdeT1) and La Saline (GdeT2)] are located on Grande-Terre Island and two [Les Salines (LD1) and La Saline (LD2)] on La Désirade Island. Map of the French Western Indies is issued from: http://www.monguidevoyages.com/caraibes.html; those from Grande-Terre and La Désirade are issued from: http://www.geoportail.gouv.fr/.

Fig. 3. Relative abundances (%) of the different iGDGTs and brGDGTs in both CL and IPL fractions. Mean values and standard errors are presented for the four water ponds investigated.

Fig. 4. Downcore profiles of absolute concentrations (µg g-1 organic carbon) in CL and IPL GDGTs and of iGDGT- and brGDGT-derived proxies in the four ponds investigated. The CBT could not be calculated in the samples from la Grande Saline.

Fig. 5. Relative abundance of caldarchaeol with respect to total iGDGTs (left axis) and values of the ACE index (right axis) vs. salinity. Mean values and standard errors in the CL and IPL fractions are presented for the four ponds investigated: Les Salines (LD1), La Saline (LD2), La Salinette (GdeT1) and la Grande Saline (GdeT2). Error bars are included in the symbols of the ACE values for Les Salines, La Saline and La Grande Saline.

Fig. 6. Comparison of brGDGT-derived temperatures based on soil (Weijers et al., 2007; Peterse et al., 2012) and lacustrine (Tierney et al., 2010; Pearson et al., 2011; Loomis et al., 2012) calibrations, and of iGDGT-derived temperatures based on lacustrine (Powers et al., 2010) and marine (Kim et al., 2008) calibrations. Mean values and standard errors of temperature estimates in (a) CL and (b) IPL fractions are presented for the four ponds investigated. The dashed line shows the mean annual air temperature (26 °C) recorded in the area.

Table 1. Biogeochemical characteristics of the water from the four ponds at the time of sampling, and organic carbon (C_{org}) contents of the sediment samples.

Island	Sample (abbreviation)	Surface area (ha)	Temperature (°C)	Salinity	pH	C_{org} (%)
	Les Salines (LD1)		29	4	7.0	
La Désirade	0-2 cm					0.1
	2-4 cm	2.1				0.7
	4-6 cm					2.5
	La Saline (LD2)		33	8	7.5	
	0-2.5 cm					0.6
	2.5-5 cm					0.3
	5-7.5 cm	1.9				1.4
	7.5-10 cm					1.2
	10-12.5 cm					0.3
Grande-Terre	La Salinette (GdeT1)		27	41	7.5	
	2-4 cm					7.5
	6-8 cm					11.3
	10-12 cm	0.5				13.2
	14-16 cm					9.6
	16-18 cm					9.3
	18-20 cm					15.1
	La Grande Saline (GdeT2)		30	93	7.0	

	0-2 cm					2.0
	4-6 cm	0.6				1.5
	8-10 cm					0.3
	12-14 cm					0.3

Highlights

- GDGTs and archaeol in cores from 4 tropical ponds with varying salinity analyzed.
- Substantial differences in GDGT distributions between the 4 ponds, reflected in temperature estimates.
- GDGT sources have to be constrained before applying GDGT-derived proxies to saline environments.